Crystal Growth: Physics, Technology and Modeling

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Lecture 13. Growth modeling in microscale

http://w3.unipress.waw.pl/~stach/cg-2022-23/

Growth modeling – two approaches

- **Modeling in macroscale**
  - transport processes during growth (mass, energy, momentum)
  - strain in nonuniform structures
  - electric properties of electronic structures and devices
  - optical properties of optoelectronic structures and devices
  - crystal morphology

- **Modeling in atomic scale**
  - crystal structure
  - energetic properties
  - kinetic properties
  - optical transitions

Growth modeling – methods

- **Modeling in macroscale**
  - **finite difference**
  - **finite volume**
  - **finite element**

- **Modeling in atomic scale**
  - **Monte Carlo**
  - **molecular dynamics**
  - **ab initio – density functional theory (DFT)**

Monte Carlo method

- **Determination of the space of elementary events**
- **Random variable definition**
- **Determination of random variable probability distribution**
- **Sampling**
- **Determination of physical quantities**

Monte Carlo method – space of the events

Axiomatic definition of probability

Probability - measure p, defined on the set (algebra) of random events {A_i, i = 1 2 3 n}, satisfying the following relationships :

- **$p(\varnothing) = 0$, $p(E) = 1$**
- **$0 \le p(A) \le 1$**
- **$p(A \cup B) = p(A) + p(B)$** ⇒ ***excluding events*** $A \cap B = \varnothing$

Conditional probability, i.e. A occurs provided that B occurred, is :

$$P(A|B) = \frac{P(A \cap B)}{P(B)}$$

Random variable

- **Algebra {A} of random events is projected on real function. Such function is called random variable**

$$\boldsymbol{X}: \{\boldsymbol{A}\} \Rightarrow \boldsymbol{R}$$

- **Algebra {A} has probability defined, according to the above listed 3 axioms.**

$$\boldsymbol{p}: \{\boldsymbol{A}\} \Rightarrow [\boldsymbol{0}, \boldsymbol{1}]$$

Any value of random variable could be associated with the probability equal the sum of the probabilities of exclusive events for which random variable has the value X. The inverse dependence of the probability on the random variable is called probability distribution.

Probability distributions

- **Positively defined**

$$p(x) \geq 0$$

- **Normalized**

$$\sum_i p(x_i) = 1$$

- **Could be determined by measurements, e.g. energy E**

$$p(E_k) = \frac{n_k}{N}$$

where: n_k ***– number of particles within*** $[E_k, E_k + \Delta E]$ ***interval,*** N ***– total number of particles.***

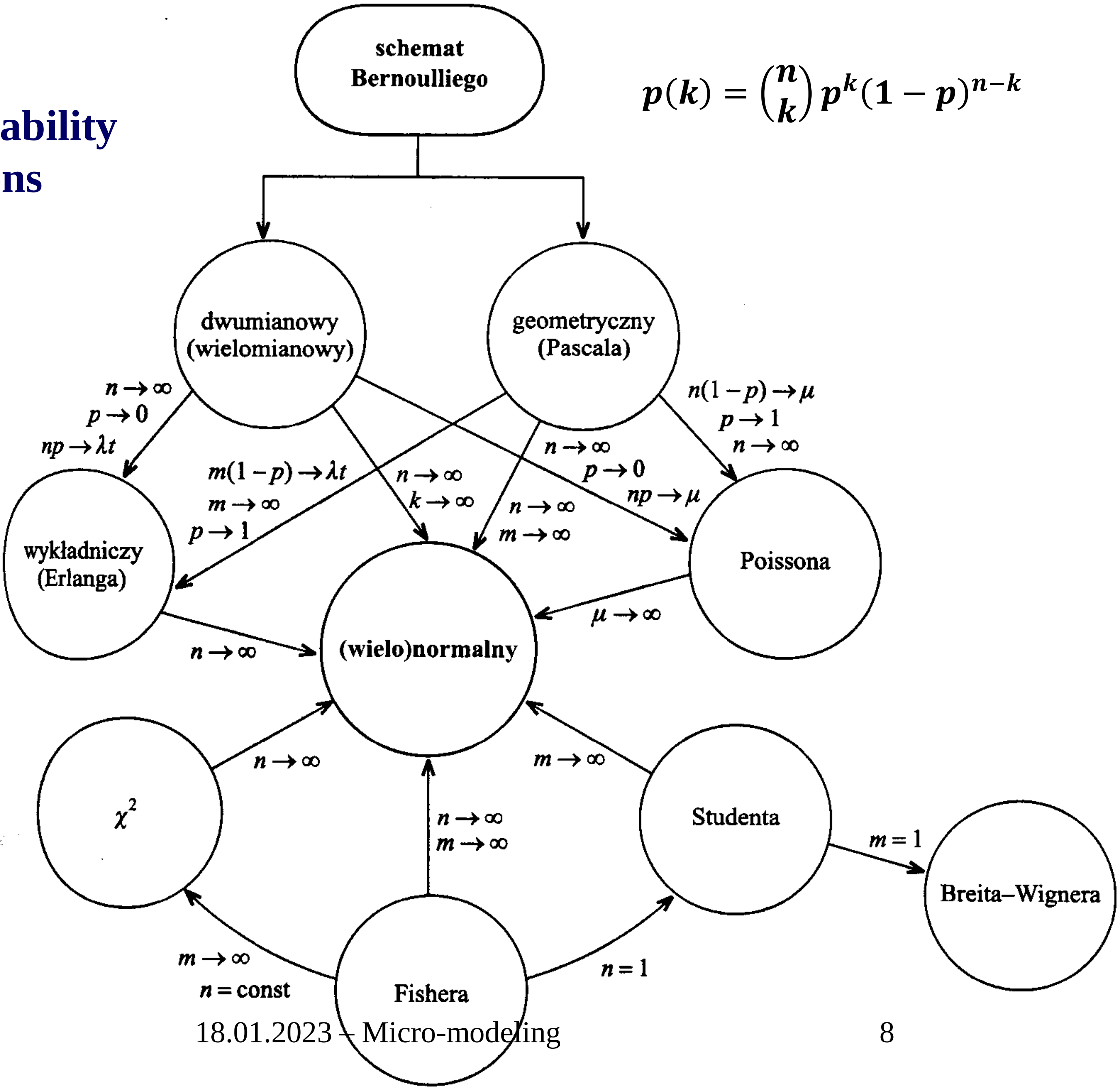
- **Continuous and discreet distributions**

Probability is called discreet when has finite number of values.

Different probability distributions

$$\int_{-\infty}^{\infty} f(x)dx = 1$$

$$p(k) = \binom{n}{k} p^k (1-p)^{n-k}$$



Sampling

Sampling – generation of random numbers of a given probability distribution of random variable (x) using numbers having uniform probability distribution (ξ).

Condition – equality of probability (equality of distributions):

$$p(x < y) = p(\xi < \xi_o) \qquad\qquad F(y) = F(\xi_o)$$

where

$$F(y) \equiv p(x < y) = \int_{-\infty}^{y} f(x)dx$$

Uniform probability distribution

$$f(\xi) = \begin{cases} 1 & \xi \in [0,1] \\ 0 & \xi \notin [0,1] \end{cases}$$

Sampling equation

$$\int_{0}^{\xi_o} d\xi = \xi_o = F(y) = \int_{-\infty}^{y} f(x)dx \qquad \Rightarrow \qquad y = F^{-1}(\xi_o)$$

Sampling

Sampling equation

$$y = F^{-1}(\xi_o)$$

Example – Lorentz distribution

$$f(x) = \frac{1}{\pi}\frac{1}{1+x^2}$$

Lorentz random variable y

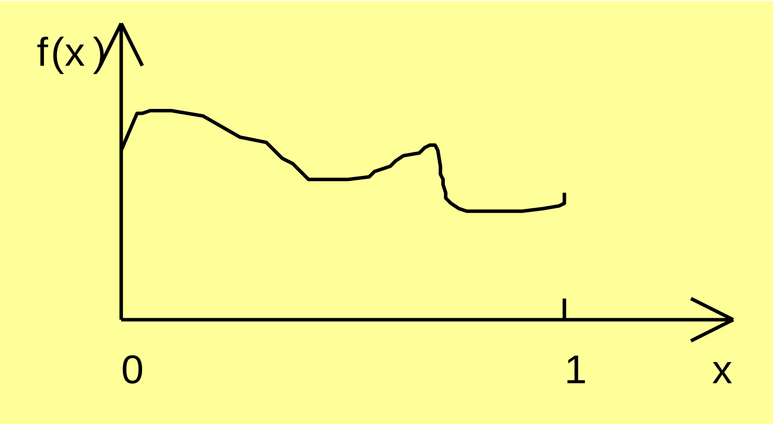
$$\int_{-\infty}^{y}\frac{dx}{\pi(1+x^2)} = \frac{artan(y)}{\pi} + \frac{1}{2} = \xi_o \quad \Longrightarrow \quad y = tan\left(\pi\xi_o - \frac{1}{2}\right)$$

Equilibrium systems (huge phase space)

- **Uniform sampling**
- **Importance sampling**

Uniform sampling - rejection techniques

Distribution function in [0,1] interval:



$$\int_0^1 f(x)dx = 1$$

Sampling by rejection technique:

- **Generation of random number ξ_1:**
- **Generation of random number ξ_2:**
- **Verification condition**

$$\xi_2 < \frac{f(\xi_1)}{max(f)} \Rightarrow x = \xi_1$$

- **Weakly convergent – large noise**
- **Reliable (no systematic error)**

Metropolis algorithm – importance sampling

Metropolis et al , J. Chem. Phys. 21 (1953) 1087

Equilibrium distribution – Gibbs canonic ensemble:

$$f(p,q) = Z^{-1}\, exp\left(-\frac{E(p,q)}{kT}\right)$$

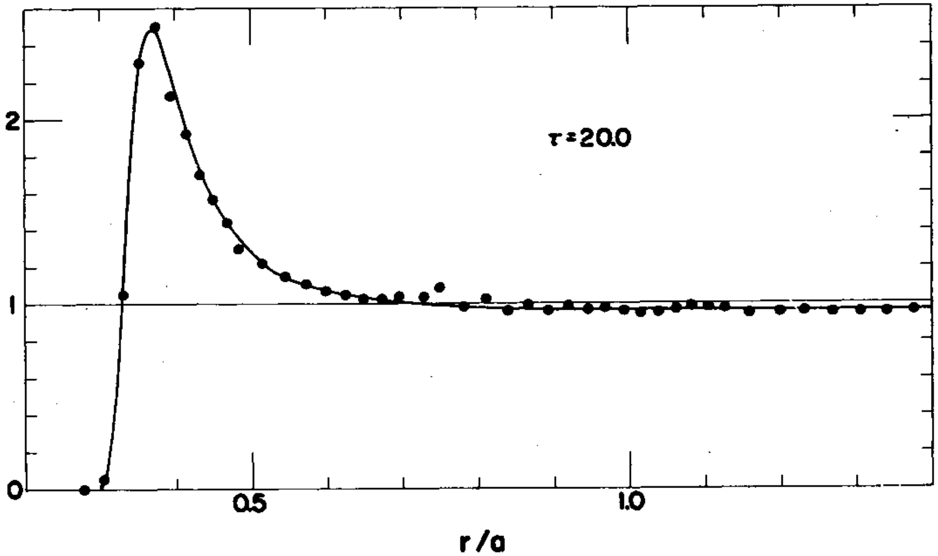
- **Initial state q(t)**
- **Next state q'(t+1)**
- **Transition probability Q**
- **Q > 1 accepted**
- **Q < 1 generation random number ξ, when ξ < Q accepted, if not it does not**

$$Q = \frac{f(q)}{f(q')} = exp\left[-\frac{E(q') - E(q)}{kT}\right]$$

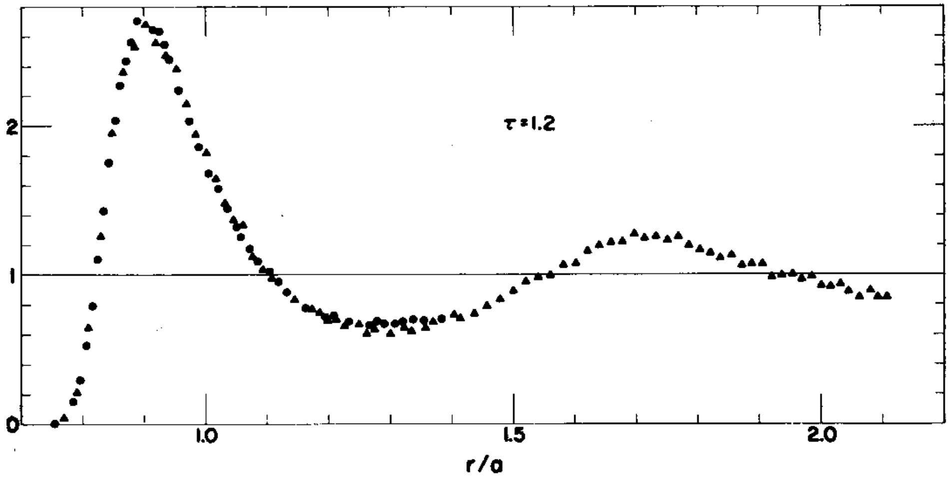
Metropolis algorithm – biased wandering in phase space

- **Strongly convergent – low noise**
- **Unreliable (prone to systematic error)**

Density – density correlation function

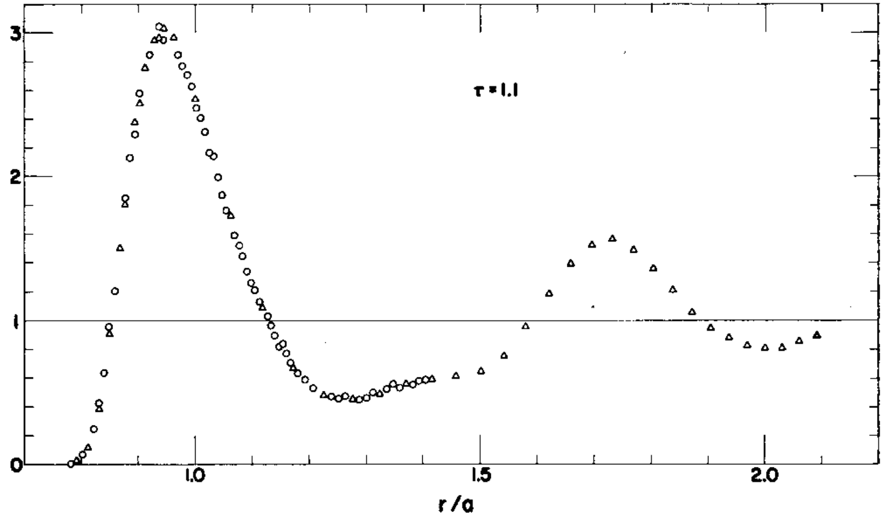


Vapor

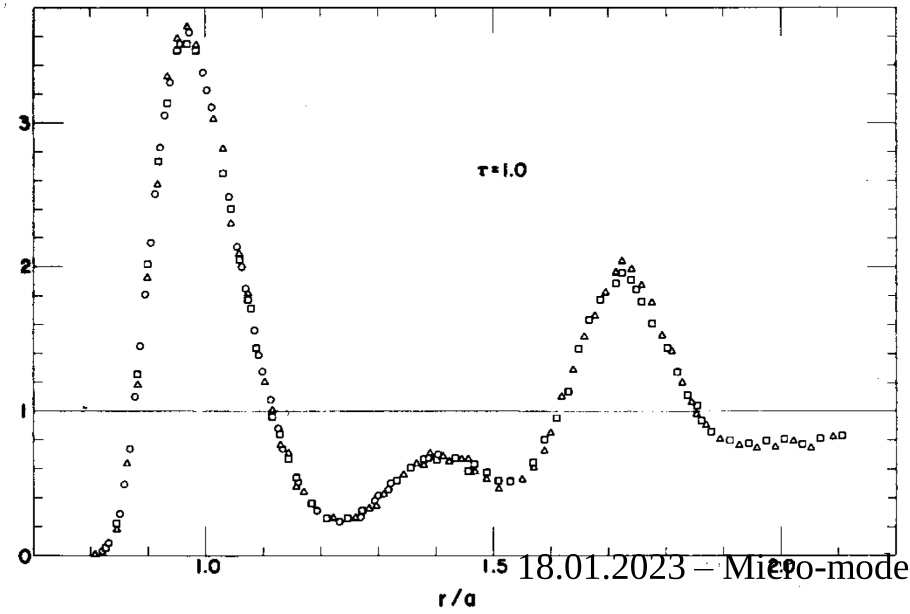


Liquid

Density – density correlation function - solid



Low density



(30a)

High density

Molecular dynamics – time integration method

Hamilton formalism

$$\dot{q} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{\partial H}{\partial q} \qquad H(p,q) = \sum_i \frac{p_i^2}{2m} + V(\{q_i\})$$

Conservative forces V = V(q)

$$p = mv \qquad m\dot{v} = F \qquad \ddot{q} = \frac{F}{m}$$

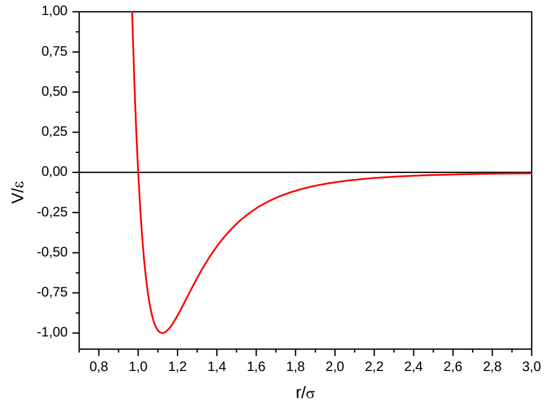
Molecular dynamics:

- **Determination of interaction potential**
- **Integration of time evolution equation**
- **Averaging**

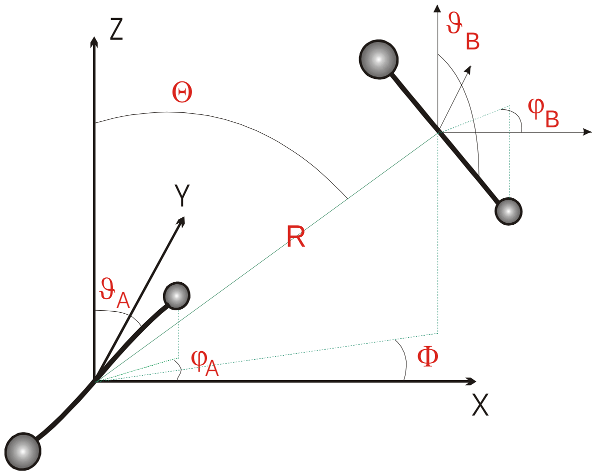
Interaction potentials

- **Lennard- Jones potential (model)**

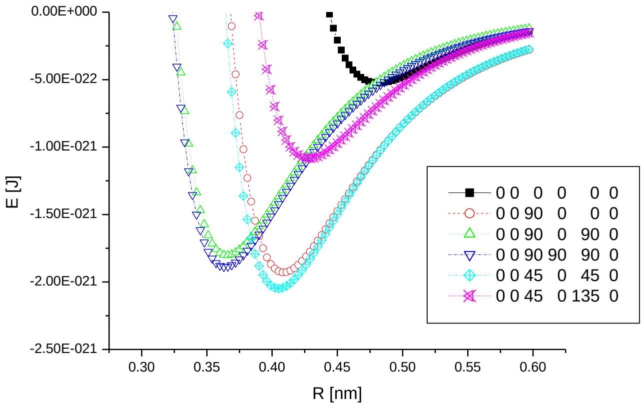
$$V(r) = \begin{cases} 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right] & r < r_c \\ 0 & r > r_c \end{cases}$$



- **Derived from QM calculations, e.g. N_2-N_2 potential**



P. Strąk – PhD (2006)



P. Strak et al. J. Chem. Phys. 126 (2007) 194501

Calculation of force – the time consuming action

Substances – interaction potentials

1. **Noble gases - pairwise Lennard-Jones interactions (short range)**
2. **Ionic crystals – pairwise Coulomb interactions (long range)**
3. **Semiconductor crystals – triple interactions (short range)**
4. **Metals – collective interactions (short range)**

Calculation of interaction potential is formidable task even at present:

- **Extremely high precision**
- **Large number of configurations**
- **Large number of distances, angles, etc.**

Integration of time evolution equation

Solution method – continuous change is represented by step-wise evolution

$$h = \Delta t = t_{n+1} - t_n$$

Open method – predictor method, e.g. Euler method Taylor series expansion

$$q_{n+1} = q_n + v_n h + \frac{1}{2} f_n h^2 \qquad v_{n+1} = v_n + f_n h$$

Fast but relatively unstable

Closed methods – predictor-corrector method, e.g. modified Euler method

Predictor

$$z_{n+1} = q_n + v_n h + \frac{1}{2} f_n h^2$$

$$f_n^* = \frac{1}{2}\left(f_n + f(z_n)\right)$$

Corrector

$$q_{n+1} = q_n + v_n h + \frac{1}{2} f_n^* h^2$$

$$v_{n+1} = v_n + f_n^* h$$

Slower (two force determination), but relatively more stable

Verlet method - workhorse

Verlet method – Taylor series expansion: forward and backward

$$q_{n+1} = q_n + q_n' h + \frac{1}{2} q_n'' h^2 + \frac{1}{6} q_n''' h^3 + O(h^4) \qquad q' \equiv \frac{\partial q}{\partial t}$$

$$q_{n-1} = q_n - q_n' h + \frac{1}{2} q_n'' h^2 - \frac{1}{6} q_n''' h^3 + O(h^4)$$

Adding both sides (velocity independent algorithm)

$$q_{n+1} = 2q_n - q_{n-1} + f(q_n) h^2$$

$$v_n = (q_{n+1} - q_{n-1})/2h$$

Leapfrog algorithm

$$q_{n+1} = q_n + v_{n+1/2} h$$

$$v_{n+1/2} = v_{n-1/2} + f(q_n) h$$

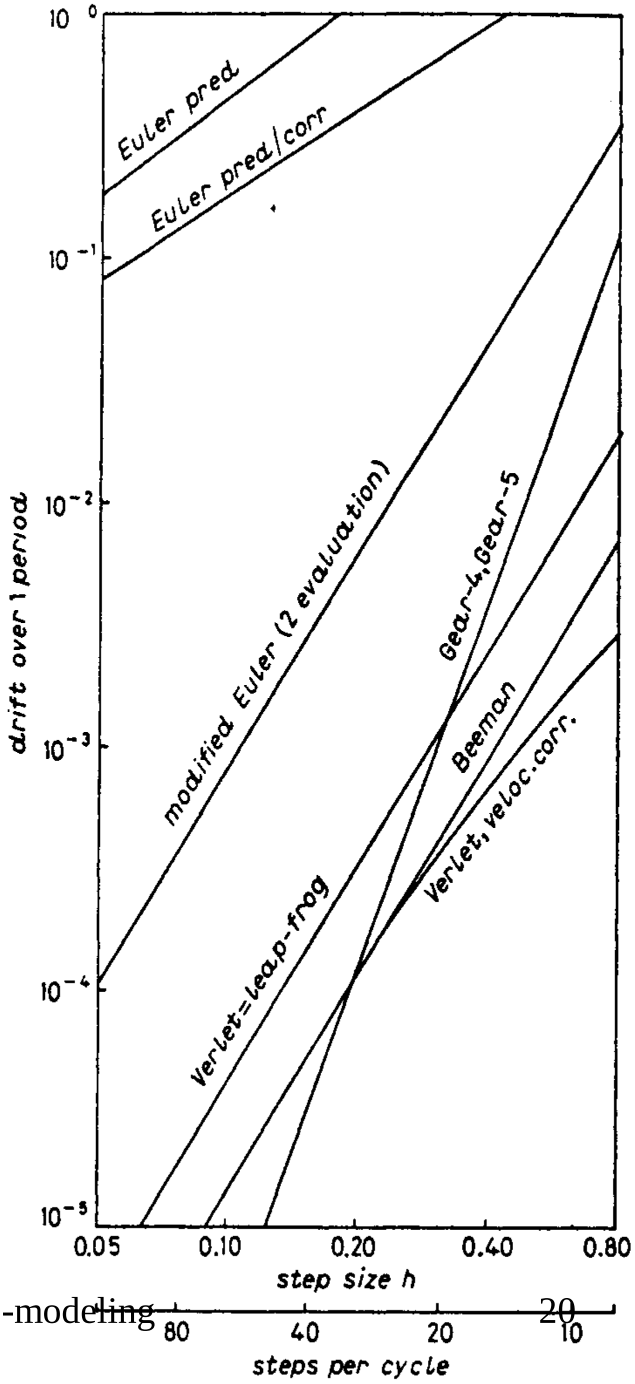
Verlet algorithm is stable, simple to implement, and of the cost of Euler method

Harmonic oscillator: coordinate comparison of various differentiation methods

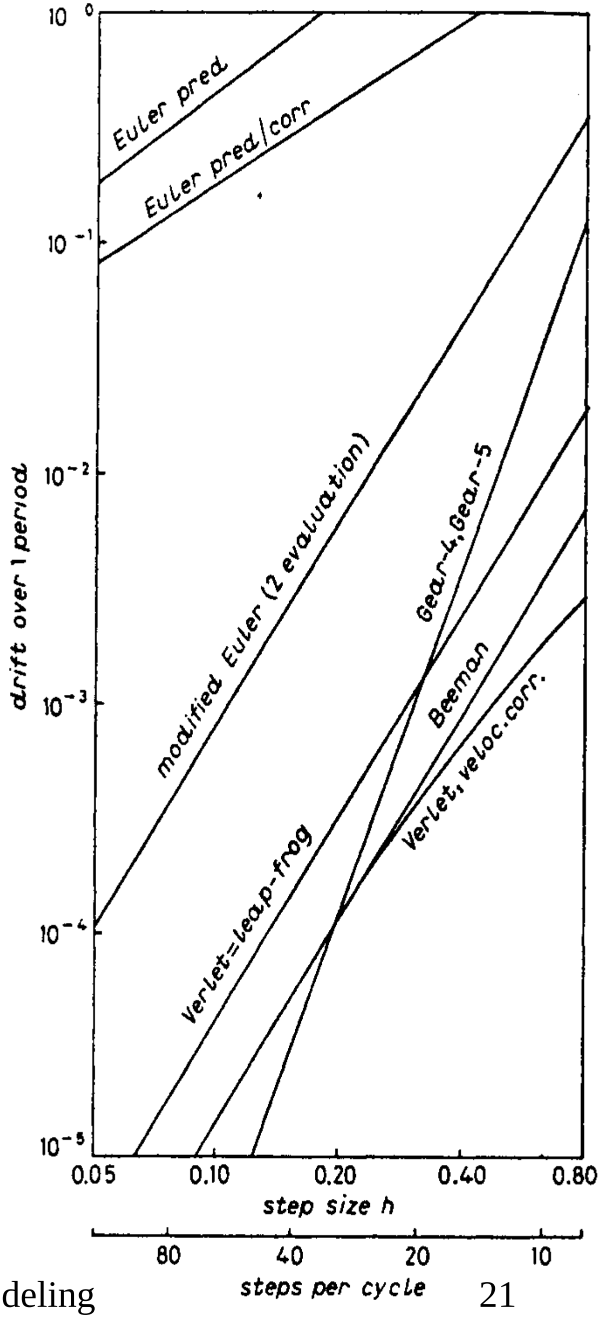
Deviation from exact solution

Steps per cycle - i

$$h = \frac{T}{i}$$



Harmonic oscillator: energy drift comparison of various differentiation methods



Steps per cycle - i

$$h = \frac{T}{i}$$

Ab initio methods – density functional theory(DFT)

- **Hamiltonian (simplest spin-less case)**

$$\hat{\boldsymbol{H}}\left(\overleftarrow{\boldsymbol{r}},\vec{\boldsymbol{R}}\right)=-\sum_{\alpha}\frac{\hbar^{2}}{2M}\Delta_{R_{\alpha}}-\sum_{i}\frac{\hbar^{2}}{2m}\Delta_{r_{i}}+\sum_{\alpha<\beta}\frac{Z_{\alpha}Z_{\beta}e^{2}}{\left|R_{\alpha}-R_{\beta}\right|}$$

$$-\sum_{i,\alpha}\frac{Z_{\alpha}e^{2}}{\left|R_{\alpha}-r_{i}\right|}+\sum_{i,j}\frac{e^{2}}{\left|r_{i}-r_{j}\right|}$$

R, M – ionic coordinates & properties
r, m – electron coordinates & properties

- **Wavefunction of the system**

$$\boldsymbol{\Psi}=\ \boldsymbol{\Psi}(\boldsymbol{R},\boldsymbol{r})$$

Adiabatic & Born-Oppenheimer approximation is used to consider atomic nuclei motion classically

System energy

$$E(R) = T + E_{N-e} + E_{e-e} + E_{N-N}$$

- **Kinetic energy :** ***T***

$$T = \frac{\left\langle \Psi(\vec{r}_1, \vec{r}_2, .. \vec{r}_N) \middle| -\sum_i \frac{\hbar^2}{2n} \Delta_{r_i} \middle| \Psi(\vec{r}_1, \vec{r}_2, .. \vec{r}_N) \right\rangle}{\langle \Psi(\vec{r}_1, \vec{r}_2, .. \vec{r}_N) | \Psi(\vec{r}_1, \vec{r}_2, .. \vec{r}_N) \rangle}$$

Kinetic energy is not represented by the density functional.

- **Nuclei interaction energy:** $E_{N\text{-}N}$

$$E_{N-N} = \sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{\left| \vec{R}_\alpha - \vec{R}_\beta \right|}$$

Nuclei interaction energy does not depend on the electron density.

System energy

$$E(R) = T + E_{N-e} + E_{e-e} + E_{N-N}$$

- **Energy of electrons – nuclei interaction:** $E_{N\text{-}e}$

$$E_{N-e} = -\frac{\left\langle \Psi(\vec{r}_1, 2..\vec{r}_N) \middle| \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} \middle| \Psi(\vec{r}_1, \vec{r}_2, ..\vec{r}_N) \right\rangle}{\langle \Psi(\vec{r}_1, \vec{r}_2, ..\vec{r}_N) | \Psi(\vec{r}_1, \vec{r}_2, ..\vec{r}_N) \rangle}$$

Electron -nuclei interaction energy is functional of the electron density.

- **Energy of electron - electron interaction:** $E_{e\text{-}e}$

$$E_{e-e} = \frac{\left\langle \Psi(\vec{r}_1, 2..\vec{r}_N) \middle| \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \middle| \Psi(\vec{r}_1, \vec{r}_2, ..\vec{r}_N) \right\rangle}{\langle \Psi(\vec{r}_1, \vec{r}_2, ..\vec{r}_N) | \Psi(\vec{r}_1, \vec{r}_2, ..\vec{r}_N) \rangle} = 2J - K$$

J and K describe electron repulsion and correlation and exchange energy.
The repulsion energy is density functional the others are not

Kohn-Sham equations

- **System energy in external field $V_{ext}(r)$ is treated as functional of electron density $E[\rho]$, which attain minimum over the space of density created by normalized wavefunctions, i.e.:**

$$\frac{\delta E[\rho]}{\delta \phi_i} = \iota_i$$

ε_j –Lagrange multiplier arising from normalization condition :

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

- **Series of nonlinear, coupled equations for wavefunctions ϕ_j**

$$\left\{ -\frac{\hbar^2}{2m} \Delta + V_{e-e} + V_{N-e} + V_{N-N} + V_{Coul} \right\} \phi_i = \varepsilon_i \phi_i$$

Kohn-Sham equation in any base χ_j

- **Wavefunction is expressed in the one-electron function base**

$$|\phi_i\rangle| = \sum_j C_{ij}|\chi\rangle$$

- **Kohn-Sham equation are translated to array equation:**

$$\sum_j H_{ij}(C)C_{jk} = \sum_j \varepsilon_i S_{ij} C_{jk}$$

$$H_{ij} = \left\langle \chi_i \middle| \left\{ -\frac{\hbar^2}{2m}\Delta + V_{e-e} + V_{N-e} + V_{N-N} + V_{Coul} \right\} \middle| \chi_i \right\rangle \qquad S_{ij} = \langle \chi_i | \chi_j \rangle$$

H depends on C, therefore this is nonlinear array equation that should be solved by the linear algebra methods as was explained.

Self-consistent field

- **Electron density**

$$\rho_{el}(\vec{r}) = \sum_i |\chi(\vec{r})|^2$$

- **Total charge density**

$$\rho_{tot}(\vec{r}) = \rho_{el}(\vec{r}) + \rho_{ion}(\vec{r}) = -e\sum_i f_{FD}(\varepsilon_i)|\chi_i(\vec{r})|_2 + e\sum_\alpha Z_\alpha \delta\left(\vec{r} - \vec{R}_\alpha\right)$$

- **Fermi-Dirac distribution function**

$$f_{FD}(\varepsilon_i) = \frac{1}{1 + exp\left(\frac{\varepsilon_i - E_F}{kT}\right)}$$

- **Poisson equation**

$$\Delta V_{Coul} = -\frac{\rho_{tot}}{\varepsilon_o}$$

Iteration equation solution (SCF loop)

I. Initial C_{ij} set

II. Calculate charge density

III. Solve Poisson equation

IV. Calculate H_{ij}

V. Solve Kohn-Sham equation – determine C_{ij}

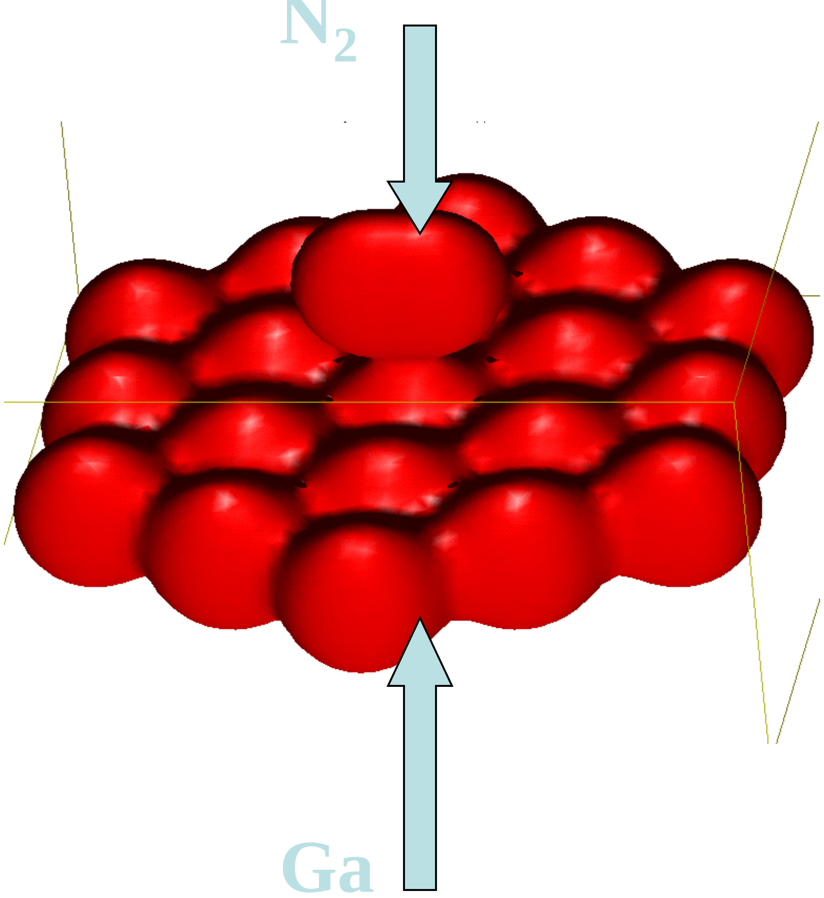
VI. Determine Fermi energy from C_{ij}

VII. Calculate charge density

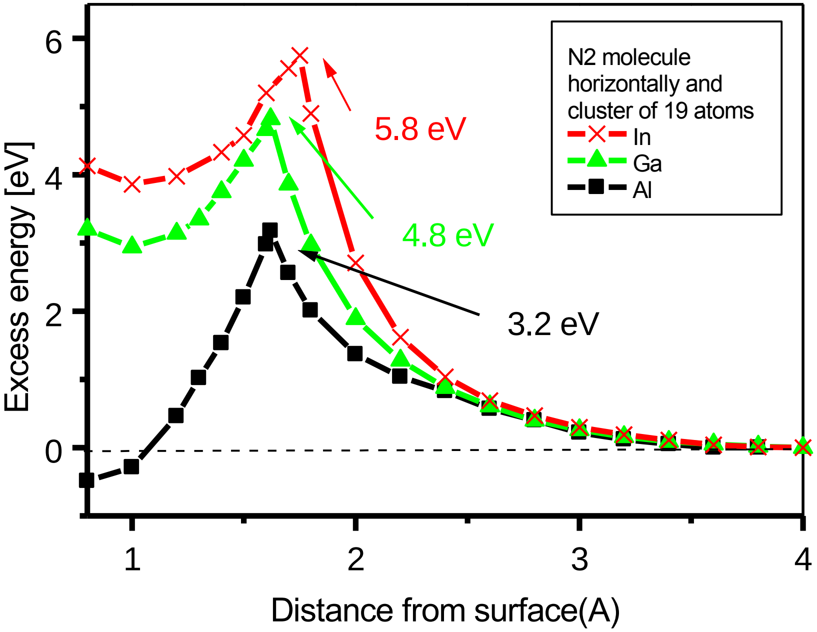
VIII. Determine convergence criterion

N_2 - Ga(l) interaction

N_2 –dissociation energy - 9.8 eV



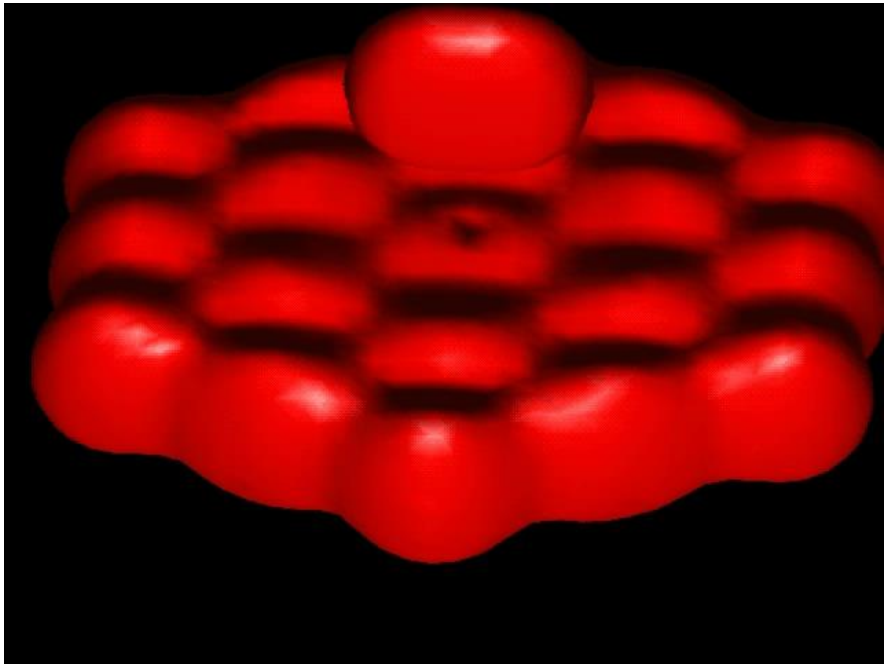
Excess energy of the system

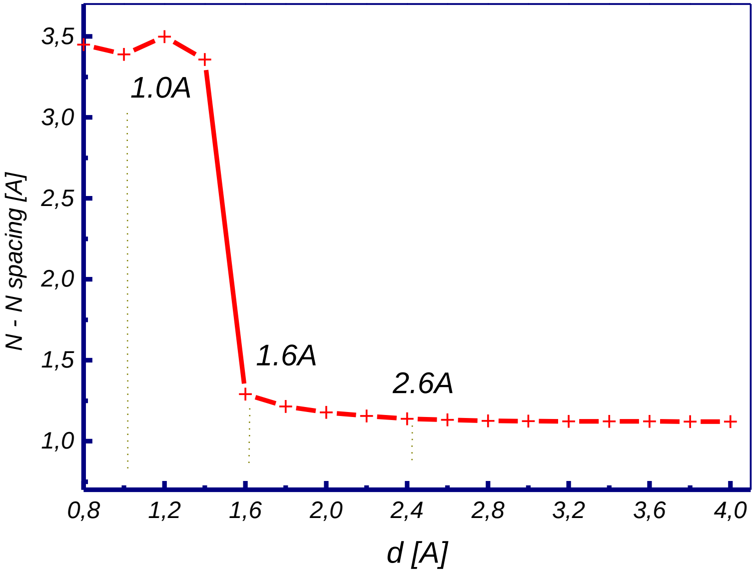


Z. Romanowski - Dmol, DFT

Z. Romanowski et al. J. Chem. Phys.
114 (2001) 6353

N_2 dissociation at Ga(l) surface



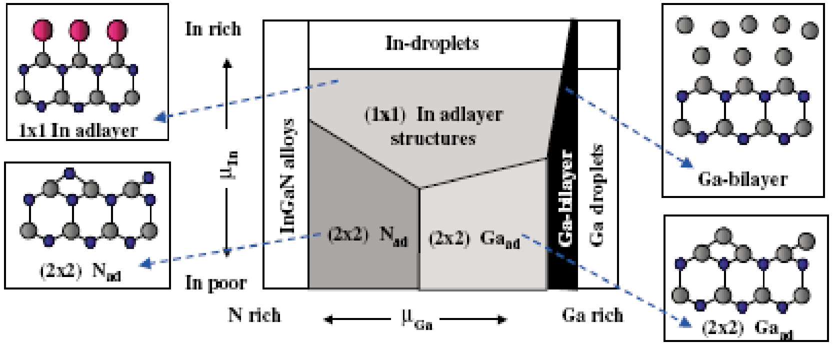


Z. Romanowski (PhD) - QM DFT

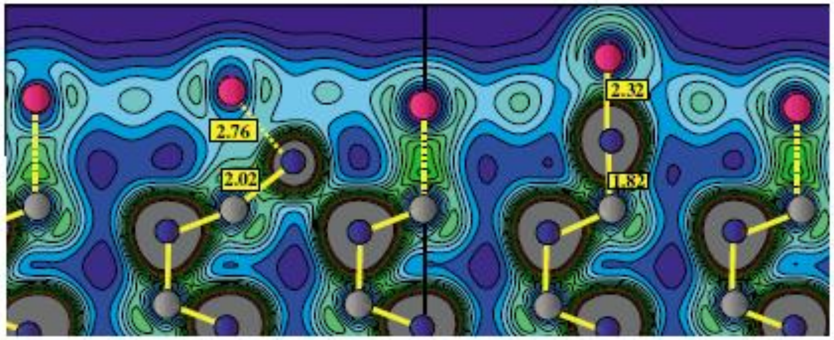
Z. Romanowski et al. J. Chem. Phys. 114 (2001) 6353

Diffusion of N at GaN(0001) surface : PA MBE

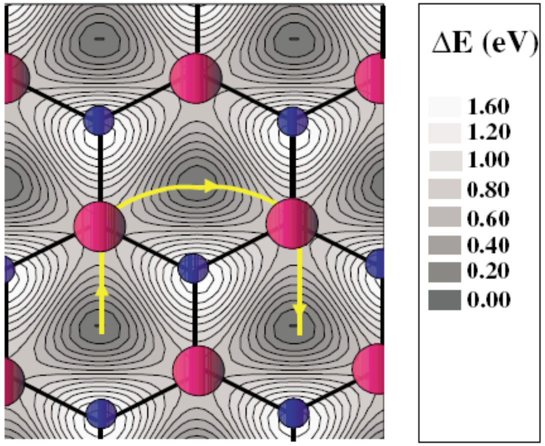
GaN (0001) surface – phase diagram



Gęstość ładunku elektronowego dla atomu N na powierzchni GaN (0001)



Energy surface for N adatom at In-covered GaN(0001) surface



Energia bariery na skok atomu N:

- powierzchnia czysta – 1.3 eV

- powierzchnia pokryta In – 0.5 eV

J. Neugebauer, et al. PRL 90 (2003) 056101

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